Compressibility of selenium glass to 5 GPa

A. K. Singh* and G. C. Kennedy

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024
(Received 26 February 1975)

The compressibility of selenium glass has been measured to 5.0 GPa by a piston-cylinder apparatus. The discontinuity in the pressure derivative of the compressibility reported by Bridgman is not observed is this study; the compression behavior is found to be normal up to 5.0 GPa. The variation of the bulk modulus $B(p)$ can be described by the relation $B(p) = B_0 + B_0'p + (1/2)B_0''p^2 + (1/6)B_0'''p^3$ with $B_0 = 8.73 \pm 0.4$ GPa, $B_0' = 7.07 \pm 0.7$, $B_0'' = -1.15 \pm 0.7$ (GPa)$^{-1}$, and $B_0''' = 0.219 \pm 0.2$ (GPa)$^{-2}$.

PACS numbers: 62.50., 62.20.D

I. INTRODUCTION

In his several investigations,[1-4] Bridgman observed that the compression of selenium glass was abnormal in that it showed a large initial compression which dropped rapidly with increasing pressure, and it exhibited a distinct break in the $(\partial^2 V/\partial^2 p)$-vs-$p$ curve in the 2.5–3.5-GPa range. Bridgman[1] called this discontinuity in curvature a transition of the third kind. Recently, Soga *et al.*[5] measured the sound velocities in selenium glass to 0.05 GPa. The pressure derivatives of the elastic moduli obtained from the sound-velocity measurements showed no anomaly. An analysis of the pressure and the temperature derivatives of the elastic moduli indicated that the data were thermodynamically self-consistent. Furthermore, using the experimental values of the bulk modulus and its pressure derivative, Soga *et al.*[5] estimated the volume compression to 5 GPa, which in the low-pressure range (below ~1 GPa) agreed well with Bridgman's[2] values, but in the high-pressure range the estimated volume compression was systematically lower than Bridgman's value, the maximum difference being about 2%. Soga *et al.*[5] pointed out that this difference could indicate a "structural change", but could not decide whether the difference was significant or not. In order to detect any anomaly in the compression curve, we decided to reexamine the compressibility of selenium glass using a piston-cylinder apparatus.

II. EXPERIMENTAL WORK

The selenium glass samples were prepared by melting selenium (99.999% purity from American Smelting Co.) in batches of nearly 20 g under vacuum in Pyrex tubes. The tube was heated to 400–500°C for 2–4 h. When the glass-melt interface was free from bubbles, the melt was allowed to cool in air. While the sample was still in the glass tube, nearly 15-mm-long slices were cut with a diamond saw. The samples could be easily pushed out of the glass tube by cooling them in a mixture of ice and NH_4Cl. We preferred the ice-NH_4Cl mixture to liquid nitrogen because samples often cracked when dipped in liquid nitrogen. The final dimensions of the sample (nearly 11 mm in diameter and 12 mm in length) were obtained by hand grinding the flat ends and the cylindrical surface.

It may be pointed out that in many other investigations, for example, in the study of atomic radial distribution functions,[6] the samples were prepared by quenching the molten selenium in ice water. We observed that on quenching in ice water, molten selenium splashes and solidifies along the wall of the tube leaving a hole along the axis of the tube. Thus, it was difficult to prepare large samples by quenching the melt in ice water. It became necessary to prepare the samples by quenching the melts in air. Similar procedures were used by Bridgman[2] and Soga *et al.*[5] It was ascertained that the selenium was glass by recording the diffracted beam intensity in the range $1.2 \leq k \leq 7.5$ Å^{-1}/ $(k = 4\pi \sin\theta/\lambda)$. A Norelco powder diffractometer fitted with a graphite monochromator in the diffracted beam was used. The radiation used was Cu$K\alpha$. The position and the relative intensities of the three peaks observed in this range agreed very well with those reported by Renninger and Averbach.[6]

The presence of pores, mainly due to trapped bubbles in the sample, vitiates the measurement of volume compression particularly in the low-pressure range. It is desirable to minimize the porosity, and hence its effect on compressibility, by carefully preparing the samples and by selecting those with minimum porosity. In this study, the densities of the samples were measured to estimate the porosity.[7] First, the density of small chips of linear dimensions of ~0.5 mm was measured relative to double-distilled water using a density bottle. The average of four measurements was 4.278 ± 0.002 g cm^{-3}. This value was taken as the density of selenium glass free from any porosity. The density of bulk selenium samples was measured by weighing them in air and in water. Out of seven samples whose densities were measured, four showed porosities of less than 0.2% and were chosen for the compressibility measurements.

The apparatus used in this work was the same as that used in earlier investigations.[8,9] Briefly, the pressure vessel consisted of a tungsten carbide (Carboloy grade 883) cylinder (1.27 cm in inside diameter, 5.08 cm in outside diameter, and 5.08 cm in length) with an interference-fitted Vascomax supporting ring. The top end of the vessel was plugged with a 1.9-cm-long tungsten carbide (Carboloy grade 999) piston. The sample was wrapped in ~0.25-mm-thick indium sheet, with 2.5-mm-thick indium disks on either end. The sample was pressurized by advancing a tungsten carbide piston into the pressure vessel from the bottom end. The extrusion of indium past the piston and the plug was prevented by pyrophyllite mitre rings. The hydraulic pressure driving the piston ram was read on a 40-cm Heise Bourdon tube gage with a stated repeatability of 0.04% of the maximum pressure used. The Heise gage reading could be easily estimated to 0.07%; this corresponded to a sensitivity of 3.6 MPa in the determination of nominal sample pressure. The piston displacement was measured with two Ames dial gages with a precision of 0.0001 cm which is about 0.02% of the maximum displacement observed.

The piston displacement versus pressure was recorded on both compression and decompression cycles. A correction was made for the piston displacement owing to various instrumental factors[8] by making another run in which the masses of indium and pyrophyllite were the same as in the selenium run, but the sample was replaced by an equal volume of CsI. A third set of measurements were made in which selenium was replaced by an equal volume of NH_4Cl. As is discussed in Sec. III, the compressibility of selenium glass was calculated using both CsI and NH_4Cl runs.

III. DATA PROCESSING

It can be easily shown from a simple consideration of the geometry of piston-cylinder apparatus that

$$\chi_s(p) = -\frac{1}{v_s}\frac{\partial v_s}{\partial p} = \frac{v_i(p)}{v_s(p)}\chi_i(p) + \frac{S(p)}{v_s(p)V(0)}\left[m_s(p) - m_i(p)\right], \tag{1}$$

where suffixes s and i denote, respectively, the sample and the standard, χ is the compressibility, $v(p) = V(p)/V(0)$, $S(p)$ is the effective area of the cross section of the piston at pressure p, $m(p)$ is the slope of the piston-displacement—vs—pressure curve, and $V(0) = V_s(0) = V_i(0)$.

The slope of the piston-displacement—vs—pressure curve for a compression (decompression) run at a given pressure is less (more) than the correct value owing to the friction of various sliding parts in the sample assembly. The slopes $m(p)$ were calculated for both compression and decompression runs from the experimental data by using the relation

$$m(p) = \frac{d(p_1) - d(p_2)}{p_1 - p_2} \tag{2}$$

where $p = \frac{1}{2}(p_1 + p_2)$ and d is the piston displacement. The correct slope at a pressure p was obtained by averaging the slopes at pressure p for the compression and decompression runs. This procedure is, of course, valid only in the pressure region in which frictional forces have completely reversed in a decompression run. Analysis of the runs in the present experiments indicated that this method of correcting frictional losses was not valid in the small region (about 0.5 GPa) terminating at the highest pressure. The samples were taken to 5.5 GPa during a compression run, so that the slopes up to 5 GPa could be obtained by this procedure. The values of $\chi_i(p)$ and $v_i(p)$ were calculated using $B_0 = 17.3$ GPa, $B_0' = 6.48$, and $B_0'' = -0.568$ $(\mathrm{GPa})^{-1}$ (Bridgman's values are quoted in Ref. 10) for ammonium chloride, and for CsI, $B_0 = 11.89$ GPa, $B_0' = 5.87$, and $B_0'' = -0.507$ $(\mathrm{GPa})^{-1}$ from the work of Barsch and Chang.[11] $S(p)$ was determined as discussed by Vaidya and Kennedy.[12] The values of $\chi_s(p)$ were calculated using Eq. (1). To start with, the Bridgman[2] values for $v_s(p)$ corrected for density[13] were used. A polynomial of the form

$$\chi_s(p) = \chi_0 + \chi_0' p + \tfrac{1}{2}\chi_0'' p^2 + \tfrac{1}{6}\chi_0''' p^3 \tag{3}$$

was fitted to the values of $\chi_s(p)$. The following relation was then used to calculate $v_s(p)$:

$$v_s(p) = \exp[-(\chi_0 p + \tfrac{1}{2}\chi_0' p^2 + \tfrac{1}{6}\chi_0'' p^3 + \tfrac{1}{24}\chi_0''' p^4)]. \tag{4}$$

$\chi_s(p)$ were recalculated from Eq. (1) using the values of $v_s(p)$ obtained from Eq. (4); polynomial (3) was fitted to these sets of $\chi_s(p)$ values and $v_s(p)$ was recalculated. Two cycles of iteration gave values of $v_s(p)$ which did not change on further iteration.

The procedure adopted here for data processing is slightly different from those adopted in our earlier investigation,[7,8] wherein the piston-displacement—vs—pressure data for compression and decompression runs were fitted to a polynomial and the smoothed data were corrected for friction. The $v_s(p)$ values were calculated from the piston-displacement—vs—pressure data. The zero-pressure compressibility and its pressure derivative were obtained by fitting a polynomial to the $v_s(p)$ values. In this work, we were interested in detecting anomalies in the pressure derivative of the compressibility. Such anomalies could go undetected if the raw data were smoothed by fitting a polynomial. For this reason we used Eq. (1) to calculate $\chi_s(p)$. In case of materials exhibiting normal compression, the two methods of data reduction lead to the same results.

IV. RESULTS AND DISCUSSION

The plots of the second derivatives of the piston displacement d as a function of pressure for two selenium runs, one NH_4Cl run, and one CsI run, are shown in Fig. 1. The second derivatives were calculated from the experimental d values by the use of the following relation:

$$\left(\frac{\Delta^2 d}{\Delta p^2}\right)_p = \frac{m(p_1) - m(p_2)}{p_1 - p_2}, \tag{5}$$

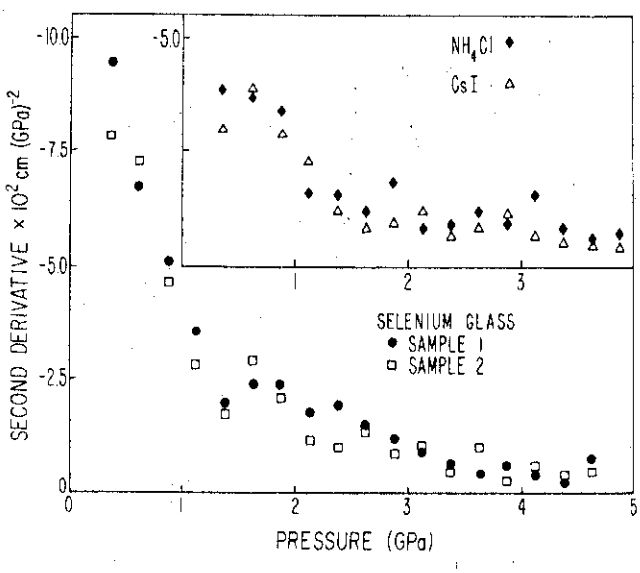

FIG. 1. $(\partial^2 d/\partial p^2)$-vs-$p$ plot for selenium glasses, NH_4Cl and CsI.

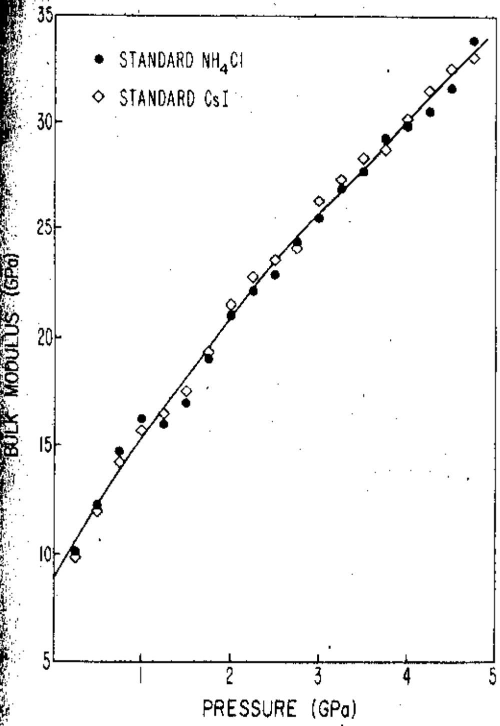

FIG. 2. A plot of the bulk modulus of selenium glass vs pressure.

where m and p are defined by Eq. (2). It is seen that, within experimental error, the second derivative decreases monotonically, and there is no indication of any discontinuity in the pressure range 2–3 GPa. Since the second $\partial^2 d/\partial p^2$ is related to $\partial^2 v/\partial p^2$, we conclude that within the experimental error there is no discontinuity in the $(\partial^2 v/\partial p^2)$-vs-$p$ curve.

The bulk modulus $B(p)$ as a function of pressure was derived from the $\chi_s(p)$ values which were obtained as was discussed in Sec. III. A plot of $B(p)$ as a function of pressure is shown in Fig. 2, and the numerical values are given in Table I. It is seen that the values of $B(p)$ obtained with the use of NH_4Cl as standard are in good agreement with those obtained with the use of CsI as standard. The zero-pressure bulk modulus B_0 and its pressure derivatives were calculated by fitting a polynomial of the form

$$B(p) = B_0 + B_0' p + \tfrac{1}{2} B_0'' p^2 + \tfrac{1}{6} B_0''' p^3. \tag{6}$$

TABLE I. Bulk modulus and volume compression of selenium glass as a function of pressure. Note that $v_s(p) = V/V_0$.

p (GPa)	$B(p)$ Standard NH_4Cl	$v_s(p)$ Standard NH_4Cl	$B(p)$ Standard CsI	$v_s(p)$ Standard CsI	$B(p)$ Average	$v_s(p)$ Average
0.25	10.1	0.9746	9.9	0.9747	10.0	0.9747
0.50	12.3	0.9543	12.0	0.9529	12.2	0.9536
0.75	14.8	0.9358	14.2	0.9340	14.5	0.9349
1.00	16.3	0.9194	15.7	0.9176	16.0	0.9185
1.25	16.0	0.9049	16.5	0.9031	16.3	0.9040
1.50	17.0	0.8920	17.7	0.8903	17.4	0.8912
1.75	19.1	0.8803	19.4	0.8788	19.3	0.8796
2.00	21.0	0.8696	21.5	0.8683	21.3	0.8690
2.25	22.1	0.8596	22.7	0.8586	22.4	0.8591
2.50	22.8	0.8504	23.5	0.8496	23.2	0.8500
2.75	24.3	0.8416	24.0	0.8411	24.2	0.8414
3.00	25.5	0.8333	26.4	0.8329	26.0	0.8331
3.25	27.0	0.8253	27.5	0.8251	27.3	0.8252
3.50	27.9	0.8177	28.5	0.8175	28.2	0.8176
3.75	29.4	0.8103	28.8	0.8102	29.1	0.8103
4.00	29.9	0.8032	30.2	0.8032	30.1	0.8032
4.25	30.6	0.7965	31.5	0.7969	31.1	0.7967
4.50	31.6	0.7901	32.5	0.7901	32.1	0.7901
4.75	33.9	0.7843	33.0	0.7842	33.5	0.7843
5.00		0.7790		0.7790		0.7790

The least-squares-fitted curve averaged for two sets of data is shown in Fig. 2 by solid lines. The values of B_0, B_0', B_0'', and B_0''' are listed in Table II separately for the two sets of data. In many earlier measurements of compressibility with a piston-cylinder apparatus, it was possible to measure B_0'' for highly compressible substances. For example, Vaidya and Kennedy[10] could measure B_0'' for CsI, and the value obtained by them was in good agreement with the value reported by Chang and Barsch,[11] which was obtained from the ultrasonic wave-velocity measurements in samples under pressure. In the present study, in addition to B_0' and B_0'', B_0''' is also reported. The question of whether the value of B_0''' is meaningful or not can be discussed by examining the standard deviations of the residuals at the various stages of polynomial fit. In the case of data obtained with CsI as standard, the standard deviation of the residuals was found to be 0.8, 0.5, and 0.4 GPa for first-, second-, and third-degree polynomials, respectively. In the case of data obtained with NH_4Cl as standard, the standard deviation of the residuals was 0.8, 0.6, and 0.6 for first-, second-, and third-degree polynomials, respectively. It is seen that in both cases a second-degree polynomial gives a smaller standard deviation than does

TABLE II. B_0, B_0', B_0'', and B_0''' for selenium glass.

B_0 (GPa)	B_0'	B_0'' [(GPa)$^{-1}$]	B_0''' [(GPa)$^{-2}$]	Pressure range (GPa)	Technique	Ref.
8.45	...	...	...	...	Static	14
9.11	...	...	...	...	Ultrasonic	16
9.14	...	...	...	...	Ultrasonic	17
9.16	8.5	...		0–0.5	Ultrasonic	5
9.29	3.2	...	...	0–5	Static	2
10.50	3.6	...	...	0–5	Static	2[a]
6.78	7.4	...	...	0–1	Static	15
9.02 ± 0.4[b]	6.74 ± 0.7	-1.086 ± 0.7	0.252 ± 0.2	0–5	Static	This work[c]
8.43 ± 0.4	7.40 ± 0.5	-1.214 ± 0.5	0.186 ± 0.2	0–5	Static	This work[d]
8.73	7.07	-1.150	0.219	0–5	Static	Average of 8 and 9

[a]Bridgman's (Ref. 2) data corrected for density (see Ref. 13).
[b]Probable error.
[c]Standard NH_4Cl.
[d]Standard CsI.

a first-degree polynomial. However, a third-degree polynomial does not lead to a significant improvement over a second-degree polynomial. The values of B_0''' obtained for two sets of data agree well, and for this reason alone, B_0''' are listed in Table II. It may be mentioned that the values of B_0, B_0', and B_0'' obtained by fitting a second-degree polynomial are slightly different from those obtained by fitting a third-degree polynomial. However, the difference is too small to alter any of the further discussions.

For comparison with the present values of B_0, etc., the values reported by other investigators are listed in Table II. The adiabatic bulk moduli B_S reported in the ultrasonic work[5,16,17] were converted to the isothermal bulk moduli B_T using the well-known relation

$$B_S = B_T(1 + \alpha\gamma T),$$

where α and γ, respectively, are the volume expansivity and the Grüneisen parameter. The values of 12.5×10^{-5} deg^{-1} for α and 0.88 for γ were used. It is seen that the values of B_0 obtained in this work are in good agreement with those reported by Graham and Chang,[16] Vedam *et al.*,[17] and Soga *et al.*[5]

The volume compression data of Bridgman[2] yield a value of 9.29 GPa for B_0, which is in good agreement with the present value and those obtained in ultrasonic experiments.[5,16,17] Bridgman[2] used a value of 4.875 g cm^{-3} for the density of selenium glass in the calculation of the volume compression. The density of selenium glass is 4.278 g cm^{-3}. When the compression data are recalculated[13] using the correct value of the density of selenium glass, a value of 10.5 GPa for B_0 is obtained; this value is significantly higher than the values obtained from the ultrasonic work. However, it is not clear, at this stage, why Bridgman's data, based on a grossly wrong density, yield a value of B_0 which agrees with the values obtained in more precise experiments viz the ultrasonic experiments. The corresponding value of B_0' is much smaller than obtained in this work or in the ultrasonic work.[5] The compression data reported by Weir[15] give a value of 6.78 GPa for B_0, which considerably lower than the present value.

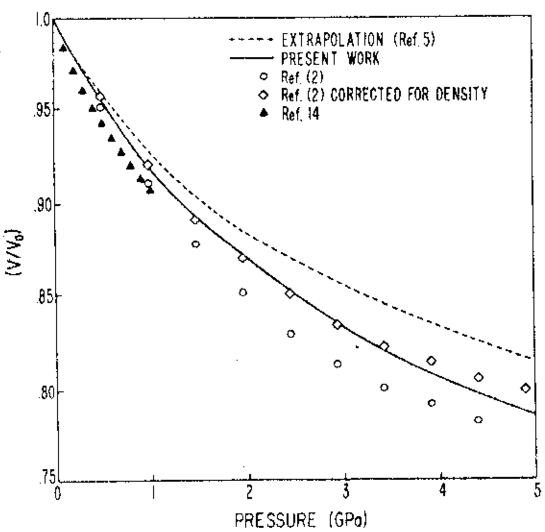

FIG. 3. A comparison of the compression data obtained by various investigators.

The volume compressions as functions of pressure obtained in this work are listed in Table I. It must be noted that the values of $v_s(p)$ listed in Table I do not reflect experimental errors, since these are calculated using Eq. (4). In fact, the scatter due to the experimental errors is reflected in the $B(p)$-vs-p plot. The estimated uncertainty in the determination of $v_s(p)$ is nearly 0.2%.

A (V/V_0)-vs-p plot is shown in Fig. 3. It is seen that Bridgman's V/V_0 values are consistently lower than the values obtained in this work. However, Bridgman's V/V_0 values, recalculated by using the correct density of selenium glass, agree well with the present values in the pressure range 0–3 GPa. Bridgman's data suggest an anomaly in the pressure range 3.5–5.0 GPa in that the $\partial^2 V/\partial p^2$ becomes nearly zero. In this work such an anomaly is not observed; the (V/V_0)-vs-p curve is found to be normal in the pressure range 0–5 GPa. The V/V_0 values reported by Weir[15] are much smaller than the present value and appear to be in error. From Fig. 3, we have omitted the results of Vaidya and Kennedy[18] because their samples consisted of a mixture of hexagonal and glassy selenium.[9]

Soga *et al.*[5] extrapolated V/V_0 to 5 GPa using, in Murnaghan's equation, the values of B_0 and B_0' obtained in their experiment. The extrapolated values of V/V_0 are consistently less than the values obtained in this work, the difference at 5.0 GPa being nearly 3%. This difference between the values of Soga *et al.*[5] and the present values is to be expected since only B_0 and B_0' were used in the extrapolation whereas the present results clearly indicate that B_0'' is quite large for selenium glass. When the present value of B_0'' in the extrapolation is included, the agreement between the present V/V_0 values and the extrapolated values improves, the maximum difference being about 1.5%. This difference arises because of the fact that the values of Soga *et al.*[5] both B_0 and B_0' are larger than the present values.

ACKNOWLEDGMENTS

The authors thank I.C. Getting for many helpful discussions and a critical review of the manuscript. The authors also wish to acknowledge the help received from Joseph Cury in the polynomial fit of the data and P.W. Mirwald in the early stages of the work. Our thanks are due to L. Faus for the maintenance of the high-pressure apparatus and J. Yamane for the delicate machining jobs. The authors wish to acknowledge partial financial support from their AEC AT (04-3)-34 and Lawrence Livermore Laboratory grants.

*On leave from Materials Science Div., National Aeronautical Lab., Bangalore, India.

[1] P.W. Bridgman, Phys. Rev. 57, 237 (1940).

[2] P.W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 21 (1940).
[3] P.W. Bridgman, Phys. Rev. 60, 351 (1941).
[4] P.W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 425 (1942).
[5] N. Soga, M. Kunugi, and R. Ota, J. Phys. Chem. Solids 34, 2143 (1973).
[6] A. L. Renninger and B. L. Averbach, Phys. Rev. B 8, 1507 (1973).
[7] In the present discussion the porosity is defined by $(d_0 - d_s)/d_0$, where d_0 is the density of a sample with zero porosity and d_s is the density of the sample whose porosity is being determined.
[8] A.K. Singh and G.C. Kennedy, J. Geophys. Res. 79, 2615 (1974).
[9] A.K. Singh and G.C. Kennedy, J. Phys. Chem. Solids 35, 1545 (1974).
[10] S.N. Vaidya and G.C. Kennedy, J. Phys. Chem. Solids 32, 951 (1971).
[11] Z. P. Chang and G.R. Barsch, Phys. Rev. Lett. 19, 1381 (1967).
[12] S.N. Vaidya and G.C. Kennedy, J. Phys. Chem. Solids 31, 2329 (1970).
[13] Bridgman (Ref. 2) used a value of 4.875 g cm^{-3} for the density of selenium glass. The correct value is 4.278 g cm^{-3}. The volume compressions were recalculated using the correct value of the density. The relation between Bridgman's (Ref. 2) $\Delta V/V_0$ values and the corrected values is as follows: $(\Delta V/V_0)_{\text{correct}} = [(\Delta V/V_0) - (\Delta V/V_0)_{\text{Fe}}](4.278/4.875) + (\Delta V/V_0)_{\text{Fe}}$. $(\Delta V/V_0)_{\text{Fe}}$ appears in the above expression because iron was used as standard. The above relation is, of course, based on the assumption that the volumes of the sample and the standard were equal in two runs and that the volumes of indium pressure transmitter and other materials such as pyrophyllite rings were also kept constant.
[14] T.W. Richards, W.N. Stull, and F.N. Brink, Carnegie Inst. Wash. Publ. 76, 37 (1907).
[15] C.E. Weir, J. Res. Natl. Bur. Stand. (U.S.) 52, 247 (1954).
[16] L.J. Graham and R. Chang, J. Appl. Phys. 36, 2983 (1965).
[17] K. Vedam, D.L. Miller, and R.Roy, J. Appl. Phys. 37, 3432 (1966).
[18] S.N. Vaidya and G.C. Kennedy, J. Phys. Chem. Solids, 33, 1377 (1972).